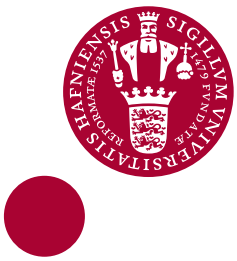

Stability of ordered phases in block copolymer melts and solutions

Mortensen, Kell

Publication date:
2009

Document version
Publisher's PDF, also known as Version of record

Ion-Containing Block Copolymer Membranes.
Moon Jeong Park[1,2] and Nitash P. Balsara[3]; [1]Department of Chemistry, POSTECH, Pohang, Korea, South; [2]Graduate Institute of Advanced Materials Science, POSTECH, Pohang, Korea, South; [3]Department of Chemical Engineering, University of California-Berkeley, Berkeley, California.

The phase behavior of ion-containing block copolymer membranes in equilibrium with humidified air is studied as a function of the relative humidity (RH) of the surrounding air, ion content of the copolymer, domain size of hydrophilic channels, and temperature. Increasing RH at constant temperature results in both disorder-to-order and order-to-order transitions. The equality of the chemical potential of water in the gas and polymer phases was exploited to determine the change in the partial molar entropy of water at phase transitions. In-situ small angle neutron scattering (In-situ SANS) experiments on the open block copolymer system, when combined with water uptake measurement indicate that the disorder-to-order transition is driven by an increase in the partial molar entropy of the water molecules in the ordered phase relative to that in the disordered phase. This is in contrast to most systems wherein increasing entropy results in stabilization of the disordered phase.

4:45 PM A2.7
Single Particle Dynamics of Water Confined in a Partially Hydrophobic Nanoporous Silica Matrix.
Antonio Faraone[1,2], Kao-Hsiang Liu[3], Chung-Yuan Mou[3], Yang Zhang[4] and Sow-Hsin Chen[4]; [1]NIST Center for Neutron Research, Gaithersburg, Maryland; [2]Department of Material Sciences and Engineering, University of Maryland, College Park, Maryland; [3]Department of Chemistry, National Taiwan University, Taipei, Taiwan; [4]Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Using three high resolution quasielastic neutron scattering spectrometers we have investigated the single particle dynamics of water confined in a hydrophobically modified MCM-41-S sample. This latter is a silica matrix containing cylindrical sieves with diameter < 20 $\AA$ arranged in a hexagonal geometry. In the hydrophobically modified sample some of the sylanol groups in the pores' wall have been substituted with methanol groups resulting in a partially hydrophobic confining surface, which could be used as a model system. In the present case, approximately 40% of the pores' wall are covered by CH_3 groups. We have been able to analyze the data in the temperature range from 300 K to 210 K using a single consistent model. Because of the heterogenous environment experienced by the water molecules in the pores, the relaxational dynamics show a broad distribution of relaxation times. However, the Fickian diffusive behaviour is retained. The obtained results help clarify the role that the chemical interaction between the water molecules and the walls of the confining host plays in determining the characteristics of the water dynamics, as compared to purely geometric constraints such as the size and shape of the pores.

5:00 PM A2.8
Bicontinuous Microemulsions Near a Planar, Hydrophilic Wall.
Michael Kerscher[1], Henrich Frielinghaus[1] and Dieter Richter[2]; [1]IFF / JCNS, Forschungszentrum Jülich GmbH, Garching, Germany; [2]IFF, Forschungszentrum Jülich GmbH, Jülich, Germany.

Microemulsions play a very important role in a multitude of industial applications. However, in many of these applications like oil production or cleaning processes, they come in contact with a variety of huge surfaces. Our studies investigate the structure of a bicontinuous microemulsion near a planar, hydrophilic wall. We observed, that a lamellar structure forms near the surface whereas the bicontinuous bulk phase stays dominant further away from the surface. Using neutron reflectometry and grazing incidence small angle neutron scattering (GISANS), we were able to record the alternating domain structure near the interface as well as the bicontinuous bulk phase. In GISANS, we used the concept of contrast variation to gain depth information about the sample: The evanescent wave travelling inside the surface at incident angles below the critical angle of total reflection decays exponentially with a penetration length $\Lambda = 1/sqrt(4\pi\Delta\rho)$. By varying the overall scattering length density of the sample, we were able to access regions at different distances of the interface. The off-specular scattering recorded in GISANS provides us with the unique possibility to directly identify the structures present in these regions. The thickness of the lamellar layer measured by neutron reflectometry confirms the GISANS measurements. The results of these experiments can be used to further understand the flow and wetting behaviour of microemulsions near surfaces.

5:15 PM A2.9
Breathable Polymer with Tunable Hydration Cushions Model Biomembrane.
Michael Jablin[1], Hillary Smith[1], Ryan Toomey[2] and Jaroslaw Majewski[1]; [1]Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]Chemical Engineering, University of South Florida, Tampa, Florida.

Neutron reflectometry reveals that a hydrated poly(N-isopropylacrylamide) network capable of a five-fold change in thickness over a 25-37°C temperature range is a novel cushion to support a single lipid bilayer in a liquid environment. The polymer swells from a collapsed-state thickness of 170 $\AA$ at 37°C to a thickness of over 900 $\AA$ at 25°C. It returns back to its collapsed state—with the bilayer intact—upon temperature increase. The hydration of the region adjacent to the membrane can be altered in situ (between 65-93 vol% water). As confirmed by neutron reflectivity, this cushioned membrane system was structurally intact after 16 days and several temperature cycles. The implications for this system are far-reaching. Polymer-cushioned bilayers promise to meet the grand challenge of developing robust, biologically relevant surrogate cellular membranes. Such a system must allow liquid access on both sides of the membrane to facilitate otherwise difficult studies ranging from lipid-protein interactions to membrane structure to membrane-based biosensors. Our results describe an extremely stable cushioned membrane system that is easy to prepare and that can be tuned to mimic the intracellular matrix.

5:30 PM A2.10
Local Structure Fluctuations of the Swollen Lamellar Phase.
Michihiro Nagao, [1]Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Cyclotron Facility, Indiana University, Bloomington, Indiana.

Amphiphilic membranes in water have been investigated to clarify mechanisms of structure formation in soft matter systems. In this work, we have focused our attention on the bilayers composed of a non-ionic surfactant, pentaethylene glycol dodecyl ether, and water. The static and dynamic structure of the membrane was measured as a function of the amount of oil, which is added to control the thickness of the bilayer, by means of small-angle neutron scattering (SANS) and neutron spin echo (NSE) techniques. The intermediate scattering function observed by NSE followed the stretched exponential function with the exponent 2/3, which is in good agreement with the single membrane fluctuation theory. In the model, the decay rate G is proportional to q^3 within the length scale ranged from the membrane thickness to the inter-membrane distance. In the present experiment, the G deviates from q^3 behavior at around q0, which corresponds to the length scale of the membrane thickness. The plot of G/q^3 vs q shows a peak at q0. This result indicates that an excess dynamic mode rather than the single membrane fluctuation mode exists at around q0. This mode could be the local structure fluctuation mode of membrane, which is related to the molecular protrusions or to the membrane thickness fluctuations. From the concept of the single membrane fluctuation theory, we estimated the membrane thickness dependence of the bending modulus. In the low swelling regime, the bending modulus is larger than that of the bilayer, while with increasing the swelling ratio, it becomes smaller. Finally when the membrane thickness is large enough, the bending modulus is about a half of that of bilayer. This result suggests the following features of the surfactant membrane: The bending motion of bilayers in water depends on the amount of oil captured within the membrane. When the swelling ratio is small, the bending motion is suppressed due to the enhancement of the local structure fluctuation mode. The mode becomes smaller with further increase the amount of oil, and finally it disappears. The bending mode of bilayers becomes that of monolayers when the membrane swells enough oil. In between these extremes, both the bending mode and the local structure fluctuation mode dominate the membrane dynamics.

SESSION A3: Poster Session for Soft Condensed Matter

Tuesday Evening, May 5, 2009
5:45 PM - 8:00 PM
Ballroom ABC

A3.1
Stability of Ordered Phases in Block Copolymer Melts and Solutions.
Kell Mortensen, Natural Sciences, University of Copenhagen, Frederiksberg, Denmark.

Block copolymer melts and solutions assemblies into nano-sized objects that order into a variety of phases, depending on molecular

parameters and mutual interaction. Beyond the classical phases of lamella ordered sheets, hexagonally ordered cylinders and cubic ordered spheres, the complex bicontinuous gyroid phase and the modulated lamellar phase are observed near the phase boundaries. The stability of these phases has been discussed on the basis of theoretical calculations. Here, we will review and discuss new experimental results showing that the given ordered phase depends critically on both molecular purity and mechanical treatment of the sample. While a variety of block copolymer micellar systems have been shown to undergo the liquid-to-bcc-to-fcc phase sequence upon varying micellar parameters (or temperature), we find for a purified system a different sequence, namely liquid-to-fcc-to-bcc [1]. The latter sequence is by the way the one predicted for pure block copolymer melts. External fields like shear or stress may also affect the ordered phase. Applying well-controlled large-amplitude oscillatory shear can be used to effectively control the texture of soft materials in the ordered states. As an example, we present results on a body-centered-cubic phase of a block copolymer system, showing how a given textures can be controlled with the application of specific shear-rate and shear-amplitude [2,3]. Shear may however also affect the thermodynamic ground state, causing shear induced ordering and disordering (melting), and shear-induced order-order transitions. We will present data showing that the gyroid state of diblock copolymer melts is unstable when exposed to large amplitude/frequency shear, transforming into the hexagonal cylinder phase [4]. The transformation is completely reversibly. With the rather slow kinetics in the transformation of copolymer systems, it is possibly in detail to follow the complex transformation process, where we find transient ordered structures[5]. 1) K Mortensen, W Batsberg, S Hvidt Macromolecules 41,1720 (2008). 2) K Mortensen, E Theunissen, R Kleppinger, K Almdal, H. Reynaers. Macromolecules 35, 7773 (2002) 3) K. Mortensen J. Polymer Science B: Polymer Physics, 42, 3095 (2004) 4) R. Eskimergen, K. Mortensen, M.E. Vigild. . Macromolecules 38, 1286 (2005) 5) K. Mortensen, M.E. Vigild. Macromolecules (2009)

A3.2

Pickering Emulsion Stability and Interfacial Structure.
Kjersta Larson-Smith and Danilo C Pozzo; Chemical Engineering, University of Washington, Seattle, Washington.

The interfacial structure and stability of hexadecane in water emulsions stabilized by silica nanoparticles are the focus of this study. These Pickering emulsions are examined using a combination of x-ray and neutron scattering and microscopy. Small angle x-ray scattering (SAXS) provides the ability to study the structure of particles at the oil-water interface. The arrangement of particles at the interface can be correlated to the stability and drop coalescence of the emulsions. Microscopy is used to quantitatively relate the macroscopic stability of the emulsion to changes in the nano-scale structure. Combining the results of the two techniques give a complete picture of Pickering emulsion behavior and the physical properties that govern emulsion stability.

A3.3

Dynamic Heteterogeneity in Supercooled Water and its Relation to the Dynamic Crossover Phenomenon.
Yang Zhang[1], Marco Lagi[1,2], Song-Ho Chong[3], Emiliano Fratini[2], Piero Baglioni[2], Eugene Mamontov[4] and Sow-Hsin Chen[1]; [1]Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]University of Florence, Florence, Italy; [3]Institute of Molecular Science, Okazaki, Japan; [4]Spallation Neutron Source, Oak Ridge, Tennessee.

The study of the dynamic heterogeneity associated with a growing dynamic length scale in the deeply supercooled regime is the focus of the field of glass-forming liquids nowadays.[1] We therefore investigated the slow dynamics of supercooled water in the 3D interconnected nanopores of aged cement paste.[2,3] Cement paste of one-week old is an ideal 3D confinement to study the dynamics of supercooled water because of the appropriate pore size to prevent freezing of water and the lack of incoherent scattering of the cement host material. By taking advantage of both the wide dynamic range and high resolution of the state-of-the-art QENS spectrometer BASIS@SNS, we are able to extract the stretched exponential self-dynamics of water molecules from 300K down to 180K. We find that: 1)A super-Arrhenius to Arrhenius dynamic crossover of the average translational relaxation time <tau> is observed at TL~230K, which coincides with a prominent peak of the specific heat. The coincidence is an evidence of the existence of the cooperatively rearranging regions described by the Adam-Gibbs theory. 2)The dynamic response function chi_T(Q,t) calculated using the experimentally determined T-dependent self-intermediate scattering function shows a peak. The peak height chi_T*(Q) increases as the temperature is lowered toward the dynamic crossover temperature TL, while decreases steadily below TL. It is a direct evidence of the enhanced dynamic fluctuations and the associated growth in size of the dynamic heterogeneity in the confined water on approaching TL from above. 3)These results are explained with an extended Model Coupling Theory by treating hopping as arising from vibrational fluctuations in the quasi-arrested state where particles are trapped inside their cages.[4] 4)Finally, we did MD simulations on TIP4P water and confirmed the above experimental results. We further calculated the four-point susceptibility chi_4(Q,t) and studied its relation with the dynamic response function chi_T(Q,t) to elucidate the concept of dynamic heterogeneity. In summary, lots of unexpected phenomena are discovered around TL, such as the crossovers in various transport properties, the peaks in thermal dynamic response functions,[5] the breakdown of the Stokes-Einstein relation,[6] and the appearance of boson peaks.[7] Our observations imply that from the point of view of changing dynamic behavior in supercooled water, the existence of the dynamic crossover temperature TL is far more important than the traditionally emphasized glass transition temperature Tg, which is about 10% lower than TL. [1]L Berthier et al, Science 310, 1797(2005) [2]Y Zhang, M Lagi, SH Chen et al, J Phys:Cond Matter 20, 502101(2008) [3]Y Zhang, M Lagi, SH Chen et al, submitted [4]Y Zhang, S-H Chong, SH Chen et al, to be published; S-H Chong, PRE 78, 041501(2008) [5]D Liu, Y Zhang, SH Chen et al, PNAS 104, 9570(2007) [6]SH Chen et al, PNAS 103, 12974(2006) [7]Y Zhang, S-H Chen et al, to be published

A3.4

Colloidal Sticky Spheres - Inter-particle Potential Spanning the Fluid/Gel Phase Transition.
Aaron Paul Rust Eberle and Norman Wagner; Chemical Engineering, University of Delaware, Newark, Delaware.

Colloidal suspensions gel to a soft solid state when interparticle attractions increase sufficiently to overcome Brownian and stabilizing forces. Gelation at lower concentrations results from formation of a percolated, space-filling network, whereas at high concentrations, an attractive driven glass forms. At intermediate concentrations, phase separation, gel formation, percolation, and glass formation are all possible states leading to solid-like behavior and the exact mechanism of dynamic arrest is often unclear. The mechanisms leading to gelation are of fundamental scientific as well as significant practical interest. In this work, we explore the microstructure of silica nanoparticle suspensions ($\sim$ 30 nm) with a thin, grafted oligomeric surface layer. In a good solvent the surface layer provides steric stability but in a poor solvent the particles aggregate. Here, the good to poor solvent transition is thermally induced creating a thermoreversible gel. Phase behavior studies, and small angle neutron scattering via contrast matching between the solvent and core particles are used to study the structure of the shell. Small angle neutron scattering and rheology are used to characterize the inter-particle potential as a function of temperature. Small angle neutron scattering, light scattering, and transition electron microscopy are employed to characterize the nano-scale and micro-scale structure of the materials. The goal of this study is to identify how the thermodynamics of the surface layer spanning the temperature range in which the solvent transitions between good and poor influences the inter-particle potential leading to gelation, and how this varies with particle concentration.

A3.5

In-situ SANS from Demixing Paraffin Blends using a Novel Rapid Heat and Quench Cell.
Stewart Andrew Pullen, Elliot Paul Gilbert and Scott Rodney Olsen; Bragg Institute, Australian Nuclear Science & Technology Organisation, Sydney, New South Wales, Australia.

Normal alkanes represent the simplest of organic compounds, yet they exhibit a rich variety of crystal structures in their pure form. For some years we have investigated the more complex situation of binary alkane blends in which mixtures have been quenched from the melt to the solid state. We have manipulated the resultant system by variation of the chain length difference between the components, molar composition, absorption into confined geometry, isotopic substitution, cooling rate and cooling depth (1). It has been shown that, for a sub-set of these blends, the systems undergo a process of local demixing to form a modulated superstructure. However, analysis of the kinetics of the demixing process has been problematic as the samples have typically had to be quenched ex-situ. The consequent time delay associated with installing the sample into the neutron beam results in a loss in the early-time data which of interest particularly to understand the physics of demixing. Work in this area has now been greatly enhanced through the development of two recent pieces of equipment designed at the OPAL research reactor in Sydney. Firstly, we have recently commissioned, Quokka, the flagship small-angle neutron scattering instrument (1). It is a 40 m pin-hole instrument with variable wavelength, focussing optics, incident beam polarisation, 1 m^2 area detector with a measured flux on sample of greater than 3 x 10^7 n cm^{-2} s^{-1} at 5 $\AA$ enabling the collection of rapid, high quality data (2). In addition, we have designed a dual temperature device that enables in-situ rapid heating and quenching of samples which are moved pneumatically between two